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(54) Title: NOVEL ADDITIVE COMPOSITION THAT REDUCES SOOT AND/OR EMISSIONS FROM ENGINES

(57) Abstract: An additive composition containing an antioxidant and a dispersant that reduces the soot content in lubricating oil in an engine and/or the emission of an engine. Further, a process for employing the additive composition to decrease the amount of soot in the lubricating oil of an engine and/or decrease the emissions from an engine.

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**Title: NOVEL ADDITIVE COMPOSITION THAT REDUCES SOOT  
AND/OR EMISSIONS FROM ENGINES**

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**Background of the Invention**

The present invention relates to a novel additive composition that decreases the amount of soot in a lubricating oil in an engine and/or decreases the amount of emissions particularly soot, hydrocarbons and/or nitrogen oxides (NO, NO<sub>2</sub>, N<sub>2</sub>O, collectively known as NO<sub>x</sub>) from an engine.

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Soot may be present in any lubricating oil used in a lubrication system of any engine that generates soot such as internal combustion engines, spark ignited engines, stationary engines, off and on highway engines and the like. Internal combustion engines, in particular diesel fueled engines, generate carbonaceous soot particles. During combustion the fuel is injected into the combustion chamber in the form of small droplets. During the combustion process, soot particles form from incompletely combusted fuel droplets. The lubricating oil for the cylinders and the rings contain the soot from the incomplete combustion process. As the pistons move up and down in the chamber, the soot particles that have formed go into the lubricating oil system of the pistons, rings, through the cylinder and into the reservoir. Accordingly, the generated soot in the engine oil contributes to problems with engine lubrication.

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Soot is also a problem in modern diesel engines with fuel injection systems. The fuel injection system has been designed to produce less emissions, but has increased the formation of soot in the lubricating oil of the engine. It further requires more frequent oil change intervals to prevent the concentration of soot particles in the oil from exceeding acceptable limits.

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The suspended soot particles in the lubricating oil have the effect of increasing the viscosity and creating wear particles in the lubricating oil. Accordingly, the soot acts like an abrasive and induces wear in the engine parts. High soot levels result in shorter drain intervals and more oil changes.

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Dispersants have been used in lubricating oils to suspend the soot build up so as to reduce the detrimental effects of the soot on engine wear. However, an oil's capacity to protect an engine is limited, even with the dispersants. In addition, soot particles are small and are finely distributed in the lubricating oil so that filters generally are not satisfactory in removing the soot. During the course of a heavy duty diesel service interval (15,000 to 30,000 miles), 5 to 10 pounds of soot is typically produced. Filtration of the suspended or dispersed soot particles in the lubricating oil is complicated by their small size of generally less than 1 micron compared to typical automotive oil filters, which are sized to remove particles which are 20 to 40 microns or greater in diameter. This level of a soot loading can not be practically filtered with conventional filtration methods.

It is desirable to decrease the concentration of particles of soot in an engine oil using a novel additive composition. It is further desirable to decrease the emissions of soot, hydrocarbons and/or NOx from an engine using a novel additive composition.

It has been found that an additive composition of the instant invention in contact with the lubricating oil of an engine can decrease the soot content in the oil as well as also reduce the emissions from an engine in particular soot, hydrocarbons and/or NOx. It has been further found that an oil based additive composition can reduce the particles of soot from the oil of an engine and/or emissions from an engine.

#### **Summary of the Invention**

In accordance with the instant invention, it has been discovered that an oil based additive composition can reduce the concentration of soot particles in a lubricating oil of an engine and/or reduce emissions from an engine.

In accordance with the present invention it has been discovered that an additive composition comprising a dispersant and an antioxidant reduces the concentration of soot in the lubricating oil of an engine and/or decreases the emissions from an engine. The additive composition can optionally contain other desired lubricant additives. The additive composition dissolves into the oil during

use of the engine. In one embodiment the release of the additive composition components is a slow release.

5 In the present invention, suspended and/or dispersed soot in engine oil is decreased by a process comprising contacting a portion of an engine oil containing the soot with the additive composition of the present invention. Further the present invention decreases the emissions from an engine by a process comprising contacting a portion of an engine oil with the additive composition of the present invention.

10 The present invention provides for the use of an additive composition to decrease the amount of suspended/dispersed soot in lubricating oil in engines and/or to decrease the emissions in particular soot, hydrocarbons and/or NOx from an engine. The engines that can use the additive composition include, but are not limited to internal combustion engines, stationary engines, generators, diesel and/or gasoline engines, on highway and/or off highway engines, two-cycle engines,  
15 aviation engines, piston engines, marine engines, railroad engines, biodegradable fuel engines and the like. In one embodiment the engine is equipped with after treatment devices, such as exhaust gas recirculation systems, catalytic converters, diesel particulate filters, NOx traps and the like.

#### **Detailed Description of the Invention**

20 In accordance with the present invention the soot concentration is decreased from a lubricating oil in an engine thereby avoiding the deleterious effects on the engine from the soot including viscosity, wear and emissions. Furthermore, the emissions of an engine is decreased by using the additive composition thereby improving the environment.

25 The additive composition is in the form of a solid, liquid, semi-solid, gel or combinations thereof. The form of the composition depends on the desired application, the mode of addition, timing of addition, the speed of release and combinations thereof.

30 The soot level and/or emissions level is reduced by contact of the lubricating oil with the additive composition. The additive composition is positioned within the lubricating system, anywhere the additive composition will be in contact with the

lubricating oil. The additive composition is positioned anywhere that the circulating oil contacts the additive composition such as full flow of oil, bypass of the oil in the reservoir or combinations therein. The location of the additive composition in the lubricating system includes but is not limited to a filter, drain pan, oil bypass loop, canister, housing, reservoir, pockets of a filter, canister in a filter, mesh in a filter, canister in a bypass system, mesh in a bypass system and the like. One or more locations can contain the additive composition. Further, if more than one additive composition is used it can be identical, similar and/or a different additive composition.

10 In one embodiment it is desirable to provide a container to hold the additive composition, such as a housing, a canister, a structural mesh or the like anywhere within the lubricating oil system, for example, a filter in a housing of an engine oil lubricating system. The necessary design feature for the container is that at least a portion of the additive composition is in contact with the oil.

15 In one embodiment, the additive composition is positioned anywhere in the filter. The filter is a desirable location to place the additive composition because the additive composition and/or spent additive composition can easily be removed, and then replaced with a new and/or recycled additive composition.

20 The additive composition needs to be in contact with the engine oil, in one embodiment the gel is in contact with the oil in the range of about 100% to about 1% of the oil in the bypass system, in another embodiment the additive composition is in contact with the oil in the range of about 75% to about 25% of the oil in the bypass system and in another embodiment the additive composition is in contact with the oil in the range of about 50% of the oil in the bypass system.

25 The release rate of the additive composition is determined primarily by the additive composition formulation. The release rate is also dependent on the form of the additive composition and/or the mode of addition. The additive composition is positioned in a location desirable for the specified and desirable dissolution rate of the additive composition. The additive composition's formulation maybe composed of one or more components that selectively dissolve completely or a portion of the components remain till the end of its service life or combinations thereof.

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The additive composition is added to the lubrication system by any known method depending on the desired form of the additive composition, the desired speed of addition, the desired release rate, the desired mode of operation and/or any of the combinations of the above. In one embodiment the additive composition is in the form of a liquid and is injected by means of a pump into the lubricating oil system. In another embodiment the additive composition is a gel and is added to the lubricating system by means of an injector pump, or a container in the oil filter. In one embodiment the additive composition is a solid and introduced into the lubricating oil system by means of an auger. In one embodiment the additive composition is a solid or semisolid and is added to the lubricating system by means of a solid addition device such as an auger..

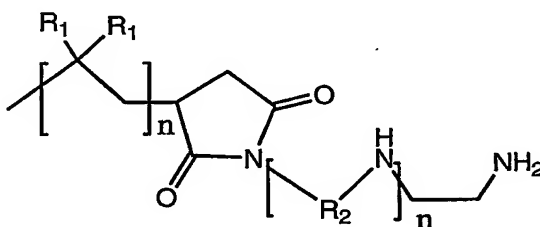
The additive composition comprises a dispersant and an antioxidant. Further the additive composition may optionally contain other lubricant additives.

The additive composition contains the dispersant in the range of about 0.1% to about 95%, in one embodiment about 5% to about 70% and in another embodiment about 7% to about 50% of the composition. The additive composition contains the antioxidant in the range of about 0.1% and about 99% in one embodiment about 5% to about 80% and in another embodiment about 10% to about 70% of the additive composition. The additive composition contains other lubricant additive in the range of about 0% to about 95%, in one embodiment about 1% to about 70% and in another embodiment about 5% to about 60% of the additive composition.

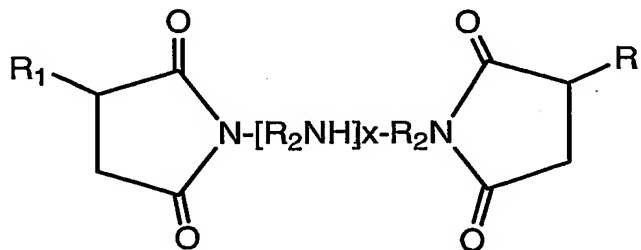
The dispersant includes but is not limited to dispersants; ashless type dispersants such as Mannich dispersants; polymeric dispersants; carboxylic dispersants; amine dispersants, high molecular weight ( $C_n$  wherein  $n \geq 12$ ) esters and the like; esterfied maleic anhydride styrene copolymers; maleated ethylene diene monomer copolymers; surfactants; emulsifiers; functionalized derivatives of each component listed herein and the like; and combinations and mixtures thereof. The dispersant can be used alone or in combination. In one embodiment the preferred dispersant is polyisobutenyl succinimide dispersant.

The dispersant includes but is not limited to ashless type dispersants such as a polyisobutenyl succinimide and the like. Polyisobutenyl succinimide ashless dispersants are commercially-available products which are typically made by reacting together polyisobutylene having a number average molecular weight ("Mn") of about 300 to 10,000 with maleic anhydride to form polyisobutenyl succinic anhydride ("PIBSA") and then reacting the product so obtained with a polyamine typically containing 1 to 10 ethylene diamine groups per molecule.

Another class of ashless dispersants includes but is not limited to high molecular weight ( $C_n$  where  $n \geq 12$ ) esters, Mannich dispersants and the like. Ashless type dispersants are characterized by a polar group attached to a relatively high molecular weight hydrocarbon chain. Typical ashless dispersants include N-substituted long chain alkenyl succinimides, having a variety of chemical structures including typically:



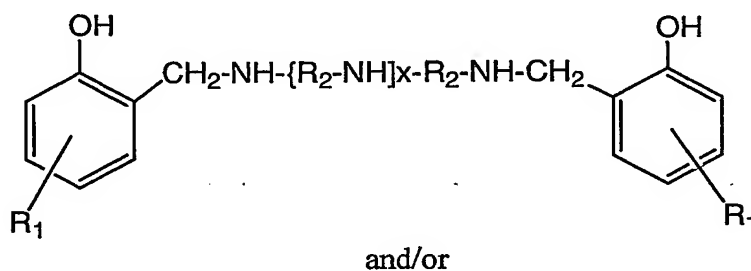
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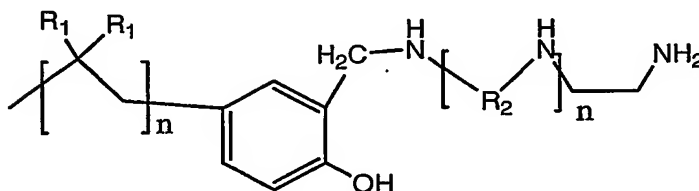
where each  $R^1$  is independently an alkyl group, frequently a polyisobutyl group with a molecular weight of 500-5000, and  $R^2$  are alkenyl groups, commonly ethylenyl ( $C_2H_4$ ) groups. Succinimide dispersants are more fully described in U.S. Patent 4,234,435 which is incorporated herein by reference. The dispersants

described in this patent are particularly effective for producing gels in accordance with the present invention.

The Mannich dispersants are the reaction products of alkyl phenols in which the alkyl group contains at least about 30 carbon atoms with aldehydes (especially formaldehyde) and amines (especially polyalkylene polyamines). Mannich bases  
5 having the following general structure (including a variety of different isomers and the like) are especially interesting.



10



Another class of dispersants is carboxylic dispersants. Examples of these “carboxylic dispersants” are described in Patent 3,219,666.

Amine dispersants are reaction products of relatively high molecular weight aliphatic halides and amines, preferably polyalkylene polyamines. Examples thereof  
15 are described, in U.S. Patent 3,565,804.

Polymeric dispersants are interpolymers of oil-solubilizing monomers such as decyl methacrylate, vinyl decyl ether and high molecular weight olefins with monomers containing polar substituents, e.g., aminoalkyl acrylates or acrylamides  
20 and poly-(oxyethylene)-substituted acrylates. Examples of polymer dispersants thereof are disclosed in the following U.S. Patents: 3,329,658, and 3,702,300.



Dispersants can also be post-treated by reaction with any of a variety of agents. Among these are urea, thiourea, dimercaptothiadiazoles, carbon disulfide, aldehydes, ketones, carboxylic acids, hydrocarbon-substituted succinic anhydrides, nitriles, epoxides, boron compounds, and phosphorus compounds.

5           Antioxidants include but are not limited to alkyl-substituted phenols such as 2, 6-di-tertiary butyl-4-methyl phenol, phenate sulfides, phosphosulfurized terpenes, sulfurized esters, aromatic amines, diphenyl amines, alkylated diphenyl amines and hindered phenols.

10           The antioxidant includes amine antioxidants and is not limited to bis-nonylated diphenylamine, nonyl diphenylamine, octyl diphenylamine, bis-octylated diphenylamine, bis-decylated diphenylamine, decyl diphenylamine and mixtures thereof.

15           The antioxidants include sterically hindered phenols and includes but is not limited to 2,6-di-tert-butylphenol, 4-methyl-2,6-di-tert-butylphenol, 4-ethyl-2,6-di-tert-butylphenol, 4-propyl-2,6-di-tert-butylphenol, 4-butyl-2,6-di-tert-butylphenol, 2,6-di-tert-butylphenol, 4-pentyl-2,6-di-tert-butylphenol, 4-hexyl-2,6-di-tert-butylphenol, 4-heptyl-2,6-di-tert-butylphenol, 4-(2-ethylhexyl)-2,6-di-tert-butylphenol, 4-octyl-2,6-di-tert-butylphenol, 4-nonyl-2,6-di-tert-butylphenol, 4-decyl-2,6-di-tert-butylphenol, 4-undecyl-2,6-di-tert-butylphenol, 4-dodecyl-2,6-di-tert-butylphenol, 4-tridecyl-2,6-di-tert-butylphenol, 4-tetradecyl-2,6-di-tert-butylphenol, methylene-bridged sterically hindered phenols include but are not limited to 4,4'-methylenebis(6-tert-butyl-o-cresol), 4,4'-methylenebis(2-tert-amyl-o-cresol), 2,2'-methylenebis(4-methyl-6-tert-butylphenol), 4,4'-methylene-bis(2,6-di-tertbutylphenol) and mixtures thereof.

25           Another example of an antioxidant is a hindered, ester-substituted phenol, which can be prepared by heating a 2,6-dialkylphenol with an acrylate ester under base catalysis conditions, such as aqueous KOH. Antioxidants may be used alone or in combination.

30           The antioxidants are typically present in the range of about 0.01% to about 95%, preferably about 0.01% to 95%, and more preferably about 1.0% to about 70% and most preferably about 5% to about 60% by weight of the gel. (Jim is this definition of antioxidant ok?)

The other lubricant additives include but are not limited to dispersants, detergents, overbased detergents, carbon black, silica, alumina, titania, magnesium oxide, calcium carbonate, lime, clay, zeolites, extreme pressure (EP) agents, wear reduction agents, viscosity index improvers, anti-foaming agents, friction reducing agents, anti-misting agents, cloud-point depressants, pour-point depressants, mineral and/or synthetic oils mixtures thereof and combination thereof. These lubricant additives components can be used alone or in combination.

The detergents include but are not limited to overbased sulfonates, phenates, salicylates, carboxylates and the like. The detergents include but are not limited to overbased calcium sulfonate detergents which are commercially-available, overbased detergents containing metals such as Mg, Ba, Sr, Na, Ca and K and mixtures thereof. The detergents may be used alone or in combination. Detergents are described, for example, in U.S. Patent 5,484,542 which is incorporated herein by reference.

The extreme pressure anti-wear additives include but are not limited to a sulfur or chlorosulphur EP agent, a chlorinated hydrocarbon EP agent, or a phosphorus EP agent, or mixtures thereof. Examples of such EP agents are chlorinated wax, organic sulfides and polysulfides, such as benzyldisulfide, bis-(chlorobenzyl) disulfide, dibutyl tetrasulfide, sulfurized sperm oil, sulfurized methyl ester of oleic acid sulfurized alkylphenol, sulfurized dispentene, sulfurized terpene, and sulfurized Diels-Alder adducts; phosphosulfurized hydrocarbons, such as the reaction product of phosphorus sulfide with turpentine or methyl oleate, phosphorus esters such as the dihydrocarbon and trihydrocarbon phosphate, *i.e.*, dibutyl phosphate, diheptyl phosphate, dicyclohexyl phosphate, pentylphenyl phosphate; dipentylphenyl phosphate, tridecyl phosphate, distearyl phosphate and polypropylene substituted phenol phosphate, metal thiocarbamates, such as zinc dioctyldithiocarbamate and barium heptylphenol diacid, such as zinc dicyclohexyl phosphorodithioate and the zinc salts of a phosphorodithioic acid combination may be used and mixtures thereof. The EP agent can be used alone or in combination.

The antifoams include but are not limited to organic silicones such as poly dimethyl siloxane, poly ethyl siloxane, poly diethyl siloxane and the like. The antifoams may be used alone or in combination.

5 The viscosity modifiers provide both viscosity improving properties and dispersant properties. Examples of dispersant-viscosity modifiers include but are not limited to vinyl pyridine, N-vinyl pyrrolidone and N,N'-dimethylaminoethyl methacrylate are examples of nitrogen-containing monomers and the like. Polyacrylates obtained from the polymerization or copolymerization of one or more alkyl acrylates also are useful as viscosity modifiers. The viscosity modifiers may be  
10 used alone or in combination.

Functionalized polymers can also be used as viscosity modifiers. Among the common classes of such polymers are olefin copolymers and acrylate or methacrylate copolymers. Functionalized olefin copolymers can be, for instance, interpolymers of ethylene and propylene which are grafted with an active monomer  
15 such as maleic anhydride and then derivatized with an alcohol or an amine. Other such copolymers are copolymers of ethylene and propylene which are reacted or grafted with nitrogen compounds. Derivatives of polyacrylate esters are well known as dispersant viscosity index modifiers additives. Dispersant acrylate or polymethacrylate viscosity modifiers such as Acryloid™ 985 or Viscoplex™ 6-054,  
20 from RohMax, are particularly useful. Solid, oil-soluble polymers such as the PIB, methacrylate, polyalkylstyrene, ethylene/propylene and ethylene/propylene/1, 4-hexadiene polymers, can also be used as viscosity index improvers. The viscosity modifiers are known and commercially available.

The friction reducing agents include but are not limited to organo-  
25 molybdenum compounds, including molybdenum dithiocarbamate. The friction reducing agents can be used alone or in combination.

The anti-misting agents include but are not limited to very high (>100,000Mn) polyolefins such as 1.5 Mn polyisobutylene (for example the material of the trade name Vistanex®), or polymers containing 2-(N-acrylamido), 2-methyl  
30 propanesulfonic acid (also known as AMPS®), or derivatives thereof. The anti-misting agents can be used alone or in combination.

The cloud point depressants include but are not limited to alkylphenols and derivatives thereof. The cloud point depressants can be used alone or in combination.

5 The pour point depressants include but are not limited to alkylphenols and derivatives thereof. The pour point depressants can be used alone or in combination.

The additive composition typically contains small amounts (about 5-40%) of base stock oils, which include but are not limited to mineral-based, synthetic or mixtures thereof.

10 Optionally, an inert carrier can be used if desired. Furthermore, other active ingredients, which provide a beneficial and desired function to the soot being decreased, can also be included in the gel. In addition, solid, particulate additives such as the PTFE, MoS<sub>2</sub> and graphite can also be included.

15 In an embodiment of this invention, the internal combustion engine is equipped with an exhaust after-treatment device. Exhaust after-treatment devices are used for modern engines to meet the new low exhaust emission standards. These systems are used to reduce undesirable emissions in the exhaust gases of internal combustion vehicle engines and are located in the exhaust system connected to the engines.

20 In one embodiment of this invention, catalysts are employed in the exhaust systems of internal combustion engines to convert carbon monoxide, hydrocarbons and nitrogen oxides (NO<sub>x</sub>) produced during engine operation into more desirable gases such as carbon dioxide, water and nitrogen. Among the broad range of available catalysts for this purpose, are oxidation catalysts, reduction catalysts and the so-called three-way converters. Oxidation catalysts can efficiently oxidize  
25 unburnt exhaust gas components and convert them into harmless substances. Three-way converters are able to simultaneously convert all three harmful substances provided that the internal combustion engine is operated close to the stoichiometric air/fuel ratio. These catalyst systems typically contain noble metals from the platinum group of the Periodic System of Elements. Particular metals used are  
30 platinum, palladium and rhodium.

In another embodiment, the exhaust after-treatment device involves a NOx trap. NOx traps, i.e. materials that are able to absorb nitrogen oxides during lean-burn operation and are able to release them when the oxygen concentration in the exhaust gas is lowered are porous support materials loaded with alkali metal or alkaline earth metals combined with precious metal catalysts such as platinum and the like.

In still another embodiment, the exhaust after-treatment device contains a diesel engine exhaust particulate filter hereinafter referred to as "DPF's". DPF's have a multiplicity of interconnected thin porous walls that define at least one inlet surface and one outlet surface on the filter and a multiplicity of hollow passages or cells extending through the filter from the inlet surface to an outlet surface. The interconnected thin porous walls allow the fluid to pass from the inlet surface to the outlet surface while restraining a desired portion of the solid particulates in the fluid from passing through. DPF's are typically installed in a housing which is inserted like a muffler or catalytic converter into the exhaust system of diesel engine equipped vehicle.

### **Specific Embodiments**

In order to more thoroughly illustrate the present invention, the following examples are provided.

#### **Gel Preparation**

A representative gel, known as Composition X is prepared by first mixing components A and C, and then adding component B with mixing in the proportions listed below. The resulting mixture is heated at 120° overnight to produce the final gel.

<u>Component</u>	<u>Chemical Description</u>	<u>% wt of Composition X</u>
A	Polyisobutenyl (2000 Mn) succinimide Dispersant	20%
B	400 TBN Overbased Alkylbenzenesulfonate Detergent	60%
C	Nonylated Diphenylamine Antioxidant	20%

**GM 6.5L Engine Test****Test Engine**

GM 6.5L Engine see ASTM D5966.

**Test Filters**

For the experimental runs, each engine was equipped with a filter with one cup into which was placed 400 g of Composition X additive gel and placed at the bottom of the filter. In the comparative runs, the same filter was used without additive gel in the cup. The additizing cup had twelve of 1/4" diameter diffusion holes at the top of the cup above the surface of the gel.

**Test Oil**

A 15W40 fully qualified (SAE-CI-4) oil was used in this test.

**Procedure**

The test vehicles was operated for 4 runs: 1) a baseline with standard filters, 2) a test run with two large hole cup filters on Truck #1 and two small-hole filters on Truck #2, 3) a second test run with two large hole cup filters on Truck #2 and two small-hole filters on Truck #1, and #4) a repeat baseline. For each run, both filters was replaced with new standard filters (Runs 1 and 4) or test filters (Runs 2 and 3). A 4-ounce sample was taken at the following mileages:

Each oil change included two flushes in which full sump quantity of new test oil and a new filter was installed, the engine was running for at least 15 minutes, and the oil drained for 30 minutes or until no more oil drips out (whichever occurred first). The two flushes were performed prior to filling with the test oil and installing a new (or test) filter; which remained on the vehicle for the next drain interval.

Oil drain samples were taken for baselines at the mileage intervals from 500-20,000 miles Initial (after vehicle is warmed up) 500 miles, 3,000 miles, 6,000 miles, 9,000 miles, 12,000 miles, and 20,000 miles.

At the 20,000-mile mark, before taking a baseline oil drain sample, test oil was flushed and oil changed and a new filter, was added, additized filter installed and initial additized filter drained.

The following analysis was performed and kinematic viscosity and 100°C (vis 100); elemental analysis by ICP, ASTM D 4739 (TBN), ASTM D664A (TAN) and percent soot by thermal gravimetric analysis (TGA).

See Designation: D 5966 – 99 “Standard Test Method for Evaluation of Engine Oils for Roller Follower Wear in Light-Duty Diesel Engine 1, AMERICAN SOCIETY FOR TESTING AND MATERIALS, 100 Barr Harbor Dr., West Conshohocken, PA 19428, from the Annual Book of ASTM Standards, copyright ASTM.

### **Results**

The results are shown in Table 1, Table 1 summarizes experiments in which the antioxidants withheld from the gel (1 Experimental, 1 Exp) compared to baselines (1 Comparatives, 1 Comp). Table 2 shows soot production with no gel in the filter, with and without dosing of a 1:1 mixture of antioxidant:dispersant throughout the 50 hr test for 2 Exp. and 2 Comp.

**Table 1. GM 6.5L Test Soot Production as a Function of Dosing with Gel Components**

Experiment	Hours on Test	0	10	20	25	30	40	50
1 Comp	% C baseline 3	0.0%	0.4%	1.2%	1.6%	1.7%	2.2%	2.8%
1 Exp	% C Gel (–AO) in filter	0.1%	0.3%	1.2%	1.5%	1.6%	2.1%	2.7%

100g alkyldiphenylamine antioxidant added at beginning of test per 7 qts of oil

**Table 2. GM 6.5L Test Soot Production as a Function of Dosing with Gel Components**

Experiment	Hours on Test	0	10	20	25	30	40	50
2 Exp	% C 1:1 AO:Disp Dosed**	0.1%	0.8%	1.5%	1.9%	2.0%	2.6%	3.3%
2 Comp	% C Baseline 4	0.1%	0.8%	1.8%	2.2%	2.2%	3.0%	3.6%

\*\*11.3g of 1:1 (wt) mixture of antioxidant (AO) and dispersant (Disp) per 7 quarts of oil added at 0, 10, 20, 30 and 40 hrs.

### **Mack T-8 Engine Test**

#### **Test Engine**

Mack T-8 Diesel Engine.

#### **Test Filters**

For these experiment runs, the engine was equipped with an oil pan with a 1" deep tray, into which was placed 400 g of Composition X additive gel. In the comparative runs, an oil pan without additive was used.

**Test Oil**

A 15W40 fully qualified (SAE-CI-4) oil was used in this test.

**Procedure**

5 A Short T-8 test was used. The Short T-8 is a modified version of the T-8/T-8E ASTM test. Conditions are shown below:

Speed (rpm): 1800      Fuel Flow (kg/hr): 63.3      Intake Manifold Temp. (C): 43

Coolant Temp. (C): 85      Crankcase Pressure (kPa): .25-.75

Inlet Air Restriction (kPa): 2.25-2.75      Exhaust Back Pressure (kPa): 3.1

10 Engine Timing (BTDC): 15 degrees

The engine timing corresponds to an average soot production rate in the 3 Comp experiment of 0.006%/hour in a 7 quart oil sump.

**Results**

15 The results are shown in Table 3, Example 3, 3 Comparative and 3 Experimental.

Table 3 demonstrates that the soot production rate is 3 Experimental is lower than in 3 Comparative, which is about the same as 3 Experimental with antioxidant. The results demonstrate that soot reduction occurs from the antioxidant and dispersant components of the additive composition (compare 3 Comparative and 20 3 Experimental) further demonstrates that the antioxidant dissolution is necessary but also the dispersant is needed.



**Table 3. Mack T-8 Test Stand Soot Levels (3 Comparative) without (3 Comparative) and with 3 Experimental Additive Gel Filter as a Function of Test Hours.**

Experiment	Hours on Test	0	7	8	10	14	20	23	24	31	32	39	40	48	56	64
3 Comp	% C, Baseline	0.05%	0.06%			0.09%		0.14%		0.22%		0.28%				
3 Exp	%C, Gel oilpan	0.05%			0.07%		0.08%				0.12%	0.21%				
3A Exp	% C, AO dose	0.10%		0.07%					0.15%				0.38%	0.50%	0.60%	0.71%

While the invention has been explained in relation to its preferred embodiments, it is to be understood that various modifications thereof will become apparent to those skilled in the art upon reading the specification. Therefore, it is to be understood that the invention disclosed herein is intended to cover such  
5 modifications as fall within the scope of the appended claims.

**We claim:**

1. An additive composition comprising a dispersant and an antioxidant used in an application selected from the group comprising decreasing the amount of soot in a lubricating oil of an engine, decreasing the amount of emissions in an engine's exhaust and combinations thereof.
2. The composition of claim 1 wherein the emissions reduced are selected from the group comprising soot, hydrocarbons and/or NO<sub>x</sub>
3. The composition of claim 1 further comprises at least one lubricant additive t selected from the group comprising detergents, overbased detergents, carbon black, silica, alumina, titania, magnesium oxide, calcium carbonate, lime, clay, zeolites, extreme pressure (EP) agents, wear reduction agents, viscosity index improvers, anti-foaming agents, friction reducing agents, anti-misting agents, cloud-point depressants, pour-point depressants, mineral and/or synthetic oils mixtures thereof and combination thereof and in the range of about 0 % to about 95 % of the additive composition.
4. The composition of claim 1 wherein the dispersant is in the range of about 0.1 % to about 95 % and the antioxidant is in the range of about 0.01 % to about 99 % of the additive composition.
5. The composition of claim 1 wherein the antioxidant is selected from the group comprising the antioxidants include but are not limited to alkyl-substituted phenols such as 2, 6-di-tertiary butyl-4-methyl phenol, phenate sulfides, phosphosulfurized terpenes, sulfurized esters, aromatic amines, and hindered phenols, is a hindered, ester-substituted phenol and combinations thereof.
6. The composition of claim 1 wherein the dispersant is selected from the group comprising ashless type dispersants such as Mannich dispersants; polymeric dispersants; carboxylic dispersants amine, dispersants, high molecular weight esters, and the like succinics; esterfied maleic anhydride styrene copolymers; maleated ethylene diene monomer copolymers; surfactants; emulsifiers; ashless succinimide, polyisbutenyl succinimide, substituted long chain alkenyl succinimides, high molecular weight esters, N-substituted long chain alkenyl succinimides, decyl

methacrylate, vinyl decyl ether, aminoalkyl acrylates, acrylamides, poly-(oxyethylene)-substituted acrylates, high molecular weight olefins with monomers containing polar substitutes; functionalized derivatives of each component listed herein; and combinations thereof.

5           7. The composition of claim 1 wherein the dispersant is selected from the group comprising ashless succinimide, polyisbutenyl succinimide, substituted long chain alkenyl succinimides, high molecular weight esters, mannich dispersants, N-substituted long chain alkenyl succinimides, carboxylic dispersants, amine  
10 dispersants, polymeric dispersants, decyl methacrylate, vinyl decyl ether, aminoalkyl acrylates, acrylamides, poly-(oxyethylene)-substituted acrylates, high molecular weight olefins with monomers containing polar substitutes and mixtures thereof; and an antioxidant selected from the group comprises alkyl-substituted phenols, 2, 6-di-tertiary butyl-4-methyl phenol, phenate sulfides, phosphosulfurized terpenes and mixtures thereof.

15           8. A process comprising contacting a portion of an engine oil with an additive composition of claim 1 resulting in the reduction of soot in the engine oil and/or emissions in an engine exhaust.

          9. The process of claim 8 wherein the additive composition is positioned to contact the oil in an area selected from the group comprising full flow oil, bypass of  
20 oil, in the reservoir and combinations thereof.

          10. The process of claim 8 wherein the additive composition is located in an area selected from the group comprising a filter, a drain pan, an oil bypass loop, a canister, a housing, a reservoir, a pocket of a filter, a canister in a filter, a mesh in a filter, a canister in a bypass system, a mesh in a bypass system and combinations  
25 thereof.

          11. The process of claim 8 wherein the additive composition is in contact with the engine oil in the range of about 100% to 1% of the engine oil.

          12. The process of claim 8 wherein the additive composition is positioned in a location of flow rate of the engine oil in the range of greater than 1% to about  
30 100% of the circulating engine oil.

          13. The process of claim 8 wherein the emissions reduced in the exhaust are

selected from the group comprising soot, NO<sub>x</sub>, hydrocarbons and combinations thereof.

14. The process of claim 8 comprising adding to the engine oil the additive composition all at the same time, a portion of the components over its service life,  
5 continuously to the engine oil over the service life of the oil and combinations thereof.

15. The process of claim 8 wherein the composition further comprises at least one lubricant additive t selected from the group comprising detergents, overbased detergents, carbon black, silica, alumina, titania, magnesium oxide,  
10 calcium carbonate, lime, clay, zeolites, extreme pressure (EP) agents, wear reduction agents, viscosity index improvers, anti-foaming agents, friction reducing agents, anti-misting agents, cloud-point depressants, pour-point depressants, mineral and/or synthetic oils mixtures thereof and combination thereof.

16. The process of claim 15 wherein the dispersant is in the range of about  
15 0.01 % to about 60 % , the antioxidant is in the range of about 0.01 % to about 60 % of and the lubricant additive is in the range of about 0 % to about 60 % of the additive composition.

17. An oil filter for an engine oil lubricating system comprising a housing, a filter for removing particulate matter from an oil bypass filter and a container with  
20 an additive composition wherein the additive composition comprises a dispersant and an antioxidant and results in the reduction of one of the following from an engine soot, NO<sub>x</sub> hydrocarbons or combinations thereof.

18. An additive composition containment device for an engine oil lubricating system comprising a housing and a container with an additive  
25 composition, and wherein the additive composition comprises a dispersant and an antioxidant for the reduction of soot from lubricating systems, engine emissions reduction or combinations thereof.

## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US2004/019802

A. CLASSIFICATION OF SUBJECT MATTER  
 IPC 7 C10M177/00 C10M163/00

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C10M

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EP0-Internal

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P,X	WO 2004/007653 A (LUBRIZOL CORP) 22 January 2004 (2004-01-22) claim 1; table 1	1-16
P,X	WO 03/104620 A (ABRAHAM WILLIAM D ; KELLEY JACK C (US); LUBRIZOL CORP (US); WILK MELOD) 18 December 2003 (2003-12-18) claim 1; table 1	1-8, 11-16
X	US 5 726 133 A (BLAHEY ALAN G ET AL) 10 March 1998 (1998-03-10) column 2, line 1 - line 54 column 4, line 16 - line 36; claim 1; table 1	1-8, 11-16
X	WO 01/44419 A (LUBRIZOL CORP ; WILK MELODY A (US)) 21 June 2001 (2001-06-21) claim 1; example 1	1-8, 11-16
-/--		

☒ Further documents are listed in the continuation of box C.

☒ Patent family members are listed in annex.

## \* Special categories of cited documents :

"A" document defining the general state of the art which is not considered to be of particular relevance

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"O" document referring to an oral disclosure, use, exhibition or other means

"P" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"&" document member of the same patent family

Date of the actual completion of the international search

28 September 2004

Date of mailing of the international search report

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## INTERNATIONAL SEARCH REPORT

Intern~~ational~~ Application No

PCT/US2004/019802

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	EP 0 462 319 A (LUBRIZOL CORP) 27 December 1991 (1991-12-27) claims 1,3-7; examples 1-3 -----	1-8, 11-16
X	US 3 336 223 A (KNEELAND PAUL D) 15 August 1967 (1967-08-15) claims 1,13; examples I,II -----	1-16
X	EP 0 416 907 A (EXXON RESEARCH ENGINEERING CO) 13 March 1991 (1991-03-13) page 4, line 13 - line 16 page 4, line 50 - line 54; claims 1,2,7,15,16 -----	1-16

# INTERNATIONAL SEARCH REPORT

International application No.  
PCT/US2004/019802

## Box II Observations where certain claims were found unsearchable (Continuation of item 2 of first sheet)

This International Search Report has not been established in respect of certain claims under Article 17(2)(a) for the following reasons:

1. ☐ Claims Nos.:  
because they relate to subject matter not required to be searched by this Authority, namely:
2. ☐ Claims Nos.:  
because they relate to parts of the International Application that do not comply with the prescribed requirements to such an extent that no meaningful International Search can be carried out, specifically:
3. ☐ Claims Nos.:  
because they are dependent claims and are not drafted in accordance with the second and third sentences of Rule 6.4(a).

## Box III Observations where unity of invention is lacking (Continuation of item 3 of first sheet)

This International Searching Authority found multiple inventions in this international application, as follows:

see additional sheet

1. ☐ As all required additional search fees were timely paid by the applicant, this International Search Report covers all searchable claims.
2. ☐ As all searchable claims could be searched without effort justifying an additional fee, this Authority did not invite payment of any additional fee.
3. ☐ As only some of the required additional search fees were timely paid by the applicant, this International Search Report covers only those claims for which fees were paid, specifically claims Nos.:
4. ☒ No required additional search fees were timely paid by the applicant. Consequently, this International Search Report is restricted to the invention first mentioned in the claims; it is covered by claims Nos.:

1 - 16

Remark on Protest

- ☐ The additional search fees were accompanied by the applicant's protest.
- ☐ No protest accompanied the payment of additional search fees.



This International Searching Authority found multiple (groups of) inventions in this international application, as follows:

1. claims: 1-16

Additive composition and process comprising contacting a portion of an engine oil with this composition.

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2. claims: 17,18

oil filter for an engine oil lubricating system and a containment device for an engine oil lubricating system.

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# INTERNATIONAL SEARCH REPORT

Information on patent family members

International Application No

PCT/US2004/019802

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
WO 2004007653 A	22-01-2004	US 2004014614 A1 WO 2004007653 A2	22-01-2004 22-01-2004
WO 03104620 A	18-12-2003	WO 03104620 A2	18-12-2003
US 5726133 A	10-03-1998	BR 9707706 A CA 2245532 A1 EP 0883667 A1 ID 16053 A WO 9731991 A1	27-07-1999 04-09-1997 16-12-1998 28-08-1997 04-09-1997
WO 0144419 A	21-06-2001	AU 2259401 A CA 2394289 A1 EP 1240282 A1 JP 2003517094 T WO 0144419 A1	25-06-2001 21-06-2001 18-09-2002 20-05-2003 21-06-2001
EP 0462319 A	27-12-1991	AT 115176 T AU 625351 B2 AU 6702390 A BR 9100628 A CA 2030481 A1 DE 69014866 D1 DE 69014866 T2 EP 0462319 A1 ES 2067640 T3 FI 910751 A JP 4261495 A NO 905227 A US 5422022 A	15-12-1994 09-07-1992 02-01-1992 07-04-1992 21-12-1991 19-01-1995 04-05-1995 27-12-1991 01-04-1995 21-12-1991 17-09-1992 23-12-1991 06-06-1995
US 3336223 A	15-08-1967	NONE	
EP 0416907 A	13-03-1991	AU 638274 B2 AU 6218890 A BR 9004414 A CA 2024005 A1 EP 0416907 A2 JP 3152196 A	24-06-1993 14-03-1991 10-09-1991 08-03-1991 13-03-1991 28-06-1991